

# Pd@Py<sub>2</sub>PZ@MSN as a Novel and Efficient Catalyst for C-C Bond Formation Reactions

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## Research Article

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# Abstract

In this paper, a novel catalyst is introduced based on the immobilization of palladium onto dipyrido[3,2-*a*:2',3'-*c*]phenazine modified mesoporous silica nanoparticles. Dipyrido[3,2-*a*:2',3'-*c*]phenazine (Py<sub>2</sub>PZ) ligand is synthesized in a simple method from the reaction of 1,10-phenanthroline-5,6-dione and 3,4-diaminobenzoic acid as starting materials. The ligand is used to functionalize mesoporous silica nanoparticles (MSN) and to modify its surface chemistry for immobilization of palladium. The palladium immobilized dipyrido[3,2-*a*:2',3'-*c*]phenazine modified mesoporous silica nanoparticles (Pd@Py<sub>2</sub>PZ@MSN) are synthesized and characterized by several characterization techniques, including TEM, SEM, FTIR, TGA, ICP, XRD, and EDS analysis. After the careful characterization of Pd@Py<sub>2</sub>PZ@MSN, the activity and efficiency of this catalyst is examined in carbon-carbon bond formation reactions. The results are advantageous in water and the products are obtained in high isolated yields. In addition, the catalyst shows very good reusability and did not show significant loss in activity after 10 sequential runs.

## Introduction

Carbon-carbon bond formation reactions, especially palladium catalyzed ones, are of significant reactions in organic chemistry. Among all the palladium catalyzed carbon-carbon bond formation reactions, Heck and Suzuki reactions have attracted interests, due to their high applications in various organic synthesis<sup>1-8</sup>. Regarding the unique advantages of Heck and Suzuki reactions, these reactions are used for the synthesis of several compounds with complex chemical structures<sup>9-13</sup>. Therefore, several efforts have been focused on the introduction of novel catalysts with improved characteristics<sup>14,15</sup>.

An interesting approach for designing of novel catalysts for Heck and Suzuki reactions is the immobilization of palladium onto modified nanoparticles. This method, enables both the advantages of homogeneous and heterogeneous catalysts. Several nanoparticles including nanosilica<sup>16,17</sup>, nitrogen rich polymers<sup>18</sup>, chitosan<sup>19</sup>, magnetic iron oxide<sup>20,21</sup>, and graphene oxide<sup>22</sup> have been used as support for palladium catalysts. Mesoporous silica nanoparticles (MSN) is an interesting ordered porous material, made of silica with high surface area and unique physical and chemical properties. MSN is chemically and physically stable and is compatible to biological systems<sup>23-25</sup>. MSNs have been used in various applications, including catalysis<sup>26,27</sup>, drug delivery<sup>28,29</sup>, tissue engineering<sup>30</sup>, and pollutant removal from air and solutions<sup>31-33</sup>. Based on the high surface area and stability and the ease of the functionalization of MSN, this family of nanoporous materials has extensively used as support for catalysts in various reactions<sup>34-37</sup>.

In this study, we introduce a novel palladium catalyst supported onto dipyrido[3,2-*a*:2',3'-*c*]phenazine modified MSN. The catalytic activity of Pd@Py<sub>2</sub>PZ@MSN is evaluated in Heck and Suzuki reactions.

## Results And Discussion

In this paper, SBA-15 MSN was synthesized by hydrothermal method and modified by (3-aminopropyl)methoxysilane. Dipyrido[3,2-*a*:2',3'-*c*]phenazine (Py<sub>2</sub>PZ) was synthesized in one step reaction between 3,4-diaminobenzoic acid and 1,10-phenanthroline-5,6-dione, which enables to react with amine groups on the surface of MSN via an amidation reaction to give Py<sub>2</sub>PZ@MSN. Pd@Py<sub>2</sub>PZ@MSN catalyst was prepared using Py<sub>2</sub>PZ@MSN as a support and it was fully characterized by various characterization techniques. The synthesis steps are presented in Scheme 1.

Electron microscopy images of Pd@Py<sub>2</sub>PZ@MSN catalyst are shown in Fig. 1. The hexagonal meso-structure of MSN-backbone could be observed in TEM image that Pd NPs appear as the dark zones (Fig. 1a). The rod like structure of MSN could clearly be observed in SEM image (Fig. 1b). In addition, EDS analysis of Pd@Py<sub>2</sub>PZ@MSN catalyst confirms the presence of Pd in the structure of the catalyst (Fig. 1c). As seen in Fig. 1d, XRD pattern of Pd@Py<sub>2</sub>PZ@MSN catalyst confirms that the crystallinity of the catalyst is similar to SBA-15<sup>38</sup>. In addition, the high angle XRD confirms the presence of Pd NPs by two peaks of 110 and 200 planes at 2θ of 39.2 and 44.3 degrees, respectively (Fig. 1d).

To confirm the successful synthesis of Pd@Py<sub>2</sub>PZ@MSN, the FT-IR spectra of nanomaterials was compared (Fig. 2a). In the FT-IR spectra of Pd@Py<sub>2</sub>PZ@MSN, a peak at 1084 cm<sup>-1</sup> represents Si-O vibrations in the structure of the catalyst. Hydroxyl groups of the catalyst could be observed at 3450 cm<sup>-1</sup> and the CH<sub>2</sub> stretching vibration are presented at 2927 cm<sup>-1</sup>. The peak appeared at 1739 cm<sup>-1</sup> is attributed to the C = O bond found in the ester moiety in the structure of Pd@Py<sub>2</sub>PZ@MSN catalyst.

The organic content in the structure of the catalyst was studied by TGA analysis (Fig. 2b). TGA curve shows that the catalyst was thermally stable up to 250°C. A weight loss at temperature of 250–350°C could be observed, which could be correlated to the degradation of organic moieties in the structure of Pd@Py<sub>2</sub>PZ@MSN catalyst. The palladium content in the structure of the catalyst was measured by ICP analysis. The results showed the Pd content in Pd@Py<sub>2</sub>PZ@MSN catalyst was 0.12 mmol.g<sup>-1</sup>.

The surface area and the pore size of Pd@Py<sub>2</sub>PZ@MSN catalyst was characterized by BET analysis and compared with MSN nanoparticles. Based on the BET and nitrogen adsorption-desorption results, Py<sub>2</sub>PZ@MSN has a high surface area of 612.37 m<sup>2</sup>.g<sup>-1</sup>. In addition, the pore diameter and pore volume of the synthesized nanoporous support are 5.14 nm and 0.72 cm<sup>3</sup>.g<sup>-1</sup>, respectively. Surface area, pore width and pore volumes of MSN are 655.37 m<sup>2</sup>.g<sup>-1</sup>, 5.75 nm, and 0.79 cm<sup>3</sup>.g<sup>-1</sup>, respectively. The decrease in surface area, pore width and pore volume of MSN by the synthesis of the catalyst is expected, while functionalization of the nanoparticles leads to such changes. The surface area and pore size results of MSN and Pd@Py<sub>2</sub>PZ@MSN catalyst are presented in Table 1.

Table 1  
Surface area and pore size results of MSN and Pd@Py<sub>2</sub>PZ@MSN catalyst.

	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Pore width (nm)	Pore volume (cm <sup>3</sup> .g <sup>-1</sup> )
MSN	655.65	5.75	0.79
Pd@Py <sub>2</sub> PZ@MSN	612.37	5.14	0.72

After the characterization of Pd@Py<sub>2</sub>PZ@MSN catalyst, the efficiency of the catalyst was examined in carbon-carbon bond formation reactions. To this purpose, Pd@Py<sub>2</sub>PZ@MSN catalyst was used in Heck and Suzuki reactions. Initially, the optimal reaction conditions were evaluated by performing the reaction under different reaction conditions including various solvents, bases, catalysts and the times of the reactions. To this end, the reaction of styrene and phenyl bromide was selected as a model reaction. The optimization results are presented in Table 2. According to the results, the best solvent for the reaction is water. However, the yields of the product were less in other solvents. Therefore, water was selected as the best solvent for the reaction. In addition, the results showed that the best yield of the product is obtained when the reaction is performed in the presence of 1 mol% of the catalyst. It should be noted that the presence of a base is critical for the reaction performance. Therefore, the reaction was performed in the presence of several bases such as triethyl amine (TEA), NaOH, KOH, and Pyridine. The results showed that TEA was the best base for the reaction. To study the role of Pd@Py<sub>2</sub>PZ@MSN catalyst in the reaction, a blank run was performed by all the reaction components except the catalyst. No product was obtained in the absence of the catalyst. Therefore, the optimized reaction conditions were selected to be water as solvent, 1.5 equivalent of triethyl amine base in the presence of 1.0 mol% of Pd@Py<sub>2</sub>PZ@MSN catalyst.

To rule out the presence of leached and homogenous Pd in the reaction mixture, in a run, the reaction was performed under the optimal reaction condition. After 60 min, the conversion of the substrates to the product measured by GC was 67%. Then, the catalyst was separated from the reaction mixture and the filtrate was stirred under the same conditions for more 60 min. The analysis of the product by GC showed that no more product has been obtained. These observations confirmed the Pd catalyst worked in the heterogeneous phase and the presence of Pd@Py<sub>2</sub>PZ@MSN catalyst was necessary for the reaction performance.

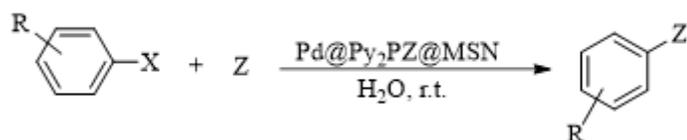
Table 2  
Optimization of the reaction of styrene and phenyl bromide in the presence of  
Pd@Py<sub>2</sub>PZ@MSN catalyst.

Entry	Solvent	Base (mol)	Catalyst (mol %)	Time(min)	Yield (%)
1	EtOH	TEA (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	61
2	MeOH	TEA (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	67
3	CH <sub>2</sub> Cl <sub>2</sub>	TEA (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	47
4	DMF	TEA (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	59
5	H <sub>2</sub> O	TEA (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	94
6	H <sub>2</sub> O	NaOH (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	80
7	H <sub>2</sub> O	KOH (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	87
8	H <sub>2</sub> O	Pyridine (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	69
9	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	77
10	H <sub>2</sub> O	No base	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	Trace
11	H <sub>2</sub> O	TEA (0.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	55
12	H <sub>2</sub> O	TEA (1.0)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	70
13	H <sub>2</sub> O	TEA (2.0)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	120	94
14	H <sub>2</sub> O	TEA (1.5)	Pd@Py <sub>2</sub> PZ@MSN (0.5)	120	46
15	H <sub>2</sub> O	TEA (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.5)	120	94
16	H <sub>2</sub> O	TEA (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	60	67
17	H <sub>2</sub> O	TEA (1.5)	Pd@Py <sub>2</sub> PZ@MSN (1.0)	150	94
18	H <sub>2</sub> O	TEA (1.5)	Pd/C (1.0)	120	56
19	H <sub>2</sub> O	TEA (1.5)	Pd(OAc) <sub>2</sub> (1.0)	"	69
21	H <sub>2</sub> O	TEA (1.5)	PdCl <sub>2</sub> (1.0)	"	61
22	H <sub>2</sub> O	TEA (1.5)	No catalyst	"	0

Reaction conditions: styrene (1 mmol); phenyl bromide (1 mmol); catalyst; solvent (5 mL); base; 25 °C.

Based on the optimized conditions, the scope and the generality of Pd@Py<sub>2</sub>PZ@MSN catalyst was studied in Heck and Suzuki reactions. The structures and the yields of the products are presented in Table 3. The high efficiency of Pd@Py<sub>2</sub>PZ@MSN catalyst in the mentioned reaction could clearly be observed. The catalyst is highly active in both Heck and Suzuki reactions and advantageous results were obtained. All substrates with electron donating and electron withdrawing functionalities have given the desired products in high isolated yields. For example, entries 4–9, 18–22, and 26–28 with phenyl halides bearing electron donating functionalities have given the products in 84–93% yields. In addition, phenyl halides bearing electron withdrawing functionalities (entries 10–14, 22–23, 29–31) have successfully participated in the reaction and have given the products in 88–99% yields. In addition, a reaction was performed with 10 mmol of the substrates to evaluate the possible scale up of the reaction. The results were advantageous and high yields of the products were obtained in the scale up reactions. The large scale reaction of iodobenzene with styrene and phenylboronic acid have led to 85% and 83% yields, respectively.

**Table 3.** The scope and generality of Pd@Py<sub>2</sub>PZ@MSN catalyst in Heck and Suzuki reactions\*



Entry	R	Z	X	Time (min)	Yield (%)	TON**	TOF***
1	H	Styrene	Br	120	94	9400	4700
2	H	Styrene	Cl	150	79	7900	3160
3	H	Styrene	I	120	96	9600	4800
4	4-Me	Styrene	Br	120	90	9000	4500
5	4-Me	Styrene	Cl	150	75	7500	3000
6	4-Me	Styrene	I	120	94	9400	4700
7	4-OMe	Styrene	Br	120	91	9100	4550
8	4-OMe	Styrene	I	120	93	9300	4650
9	4-NMe <sub>2</sub>	Styrene	Br	120	93	9300	4650
10	4-Cl	Styrene	Br	120	96	9600	4800
11	4-Cl	Styrene	Cl	150	70	8000	3200
12	4-CN	Styrene	Br	120	94	9400	4700
13	4-CN	Styrene	Cl	150	78	8800	3520
14	4-CHO	Styrene	Br	120	93	9300	4650
15	H	butyl acrylate	Br	120	96	9600	4800
16	H	butyl acrylate	Cl	150	82	8200	3280
17	H	butyl acrylate	I	90	96	9600	6400
18	4-Me	butyl acrylate	Br	120	89	8900	4450
19	4-Me	butyl acrylate	Cl	150	75	7500	3000
20	4-OMe	butyl acrylate	Br	120	91	9100	4550
21	4-OMe	butyl acrylate	Cl	150	76	7600	3040
22	4-CN	butyl acrylate	Br	120	94	9400	4700
23	4-CN	butyl acrylate	Cl	150	89	8900	3560
24	H	Ph(BOH) <sub>2</sub>	Br	120	92	9200	4600

\* Reaction conditions: styrene, butyl acrylate, or phenylboronic acid (1 mmol); phenyl halide (1 mmol); Pd@Py<sub>2</sub>PZ@MSN catalyst (1 mol%); H<sub>2</sub>O (5 mL); TEA (1.5 mmol); 25°C; \*\* TON is calculated as the number of moles of substrate converted to product divided by the number moles of palladium catalyst; \*\*\* TOF is defined as TON h<sup>-1</sup>; \*\*\*\* Scale up reactions: styrene or phenylboronic acid (10 mmol); phenyl bromide (10 mmol); Pd@Py<sub>2</sub>PZ@MSN catalyst (1 mol%); H<sub>2</sub>O (50 mL); TEA (15 mmol); 25°C.

Entry	R	Z	X	Time (min)	Yield (%)	TON**	TOF***
25	H	Ph(BOH) <sub>2</sub>	I	150	97	9700	3880
26	4-Me	Ph(BOH) <sub>2</sub>	Br	120	88	8800	4400
27	4-Me	Ph(BOH) <sub>2</sub>	I	150	92	9200	3680
28	4-OMe	Ph(BOH) <sub>2</sub>	Br	120	84	8400	4200
29	4-Cl	Ph(BOH) <sub>2</sub>	Br	120	93	9300	4650
30	4-CN	Ph(BOH) <sub>2</sub>	Br	120	95	9500	4750
31	4-CN	Ph(BOH) <sub>2</sub>	I	150	99	9900	3960
32****	H	Styrene	I	120	85	8500	4250
33****	H	Ph(BOH) <sub>2</sub>	I	120	83	8300	4150

\* Reaction conditions: styrene, butyl acrylate, or phenylboronic acid (1 mmol); phenyl halide (1 mmol); Pd@Py<sub>2</sub>PZ@MSN catalyst (1 mol%); H<sub>2</sub>O (5 mL); TEA (1.5 mmol); 25°C; \*\* TON is calculated as the number of moles of substrate converted to product divided by the number moles of palladium catalyst; \*\*\* TOF is defined as TON h<sup>-1</sup>; \*\*\*\* Scale up reactions: styrene or phenylboronic acid (10 mmol); phenyl bromide (10 mmol); Pd@Py<sub>2</sub>PZ@MSN catalyst (1 mol%); H<sub>2</sub>O (50 mL); TEA (15 mmol); 25°C.

A great advantage of Pd@Py<sub>2</sub>PZ@MSN catalyst is its reusability. To illustrate the reusability of the catalyst, after the reaction of styrene (or phenylboronic acid) and phenyl bromide was completed, the catalyst was separated by filtration. The separated catalyst was washed, dried, and used in next reaction run under the same reaction conditions. The reaction was repeated for 10 sequential reactions that the obtained results are presented in Fig. 3. It could be seen that in both Heck and Suzuki reactions, no big loss in the activity of the catalyst is observed.

To show the structural stability of the catalyst during the reaction conditions, the catalyst was separated after the 5th reaction run, washed with water and ethanol. Then, the dried 5th re-used Pd@Py<sub>2</sub>PZ@MSN catalyst was characterized by SEM and BET analysis. The results are presented in Fig. 4 and Table 4, respectively. Comparing the results of the recovered catalyst with the fresh ones confirm the good stability of the catalyst during the reactions.

Table 4  
Surface area and pore size results of the recovered Pd@Py<sub>2</sub>PZ@MSN catalyst.

Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Pore width (nm)	Pore volume (cm <sup>3</sup> .g <sup>-1</sup> )
607.21	5.09	0.70

# Experimental

## *General remarks*

All the chemicals, reagents, and solvent were purchased from Merck, Germany and Sigma, Germany. TEM images were recorded on a CM 10 Philips instrument.  $^1\text{H}$  (500 MHz) spectra were recorded on a Bruker Avance spectrometer in DMSO,  $d_6$  solution with tetramethylsilane (TMS) as an internal standard. A TESCAN T3000 instrument was applied to record the SEM images. OPTIMA7300DV ICP analyzer was applied for analyzing the palladium content of the catalyst. The FT-IR spectra were recorded on a Nicolet Magna FT-IR 550 spectrophotometer using potassium bromide disks. BET of the samples was analyzed by an ASAPTM micromeritics 2020 instrument. The particle size was measured using HORIBA SZ100-Z DLS instrument. Thermo-gravimetric Analyzer (TGA) at heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  over the temperature range of  $40\text{--}600\text{ }^\circ\text{C}$  under nitrogen atmosphere.

## *Synthesis of $\text{Py}_2\text{PZ}$ ligand*

1,10-Phenanthroline-5,6-dione (1.05 g, 5 mmol) and 3,4-diaminobenzoic acid (0.76 g, 5 mmol) were dissolved in ethanol and refluxed for 2h. The reaction progress was monitored by TLC monitoring. After the reaction completion, the solvent was evaporated and the product was purified by recrystallization from ethanol.

## *Synthesis of $\text{Pd@Py}_2\text{PZ@MSN}$ catalyst*

SBA-15 was synthesized according to previously reported method<sup>39</sup>. A mixture containing mesoporous silica nanoparticles (0.5 g) in ethanol/deionized water (1:2, 30 mL) and HCl (pH = 4) was prepared and sonicated for 30 min. A solution of (3-aminopropyl)methoxysilane (1 g) in ethanol (30 mL) was prepared and added drop-wise to the above mixture by vigorous stirring. The reaction mixture was stirred for 24 h and then, the product was separated by filtration and washed with deionized water and ethanol. The product was dried at  $70\text{ }^\circ\text{C}$  in vacuum for 12 h to obtain amine modified mesoporous SBA-15.

A mixture of amine modified mesoporous SBA-15 (0.5 g) in dichloromethane (75 mL) was sonicated for 30 min. Then, dipyrido[3,2-*a*:2',3'-*c*]phenazine-11-carboxylic acid (1.6 g, 5 mmol) in dichloromethane (25 mL), was added of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (5 mmol, 1 eq) and *N*-hydroxysuccinimide (5.5 mmol, 1.1 eq) were added. The reaction mixture was stirred overnight at room temperature. The product was separated from the reaction mixture and washed with ethanol and dried for 12 h in a vacuum oven.

The solid support (0.5 g) was added to dry acetone and sonicated for 30 min. Then,  $\text{PdCl}_2$  (1 mmol) was added and the reaction mixture was stirred at  $40\text{ }^\circ\text{C}$  under inert atmosphere for 24 h.  $\text{Pd@Py}_2\text{PZ@MSN}$  catalyst, was separated from the reaction mixture by centrifugation, washed thoroughly with EtOH and diethyl ether and dried under vacuum at room temperature for 12 h.

### *General procedure for the carbon-carbon bond formation reactions*

Phenyl halide (1 mmol), alkene (1.1 mmol, in case of Heck reaction), phenyl boronic acid (1.0 mmol, in case of Suzuki reaction), triethyl amine (1.5 mmol) and Pd@Py<sub>2</sub>PZ@MSN catalyst (1.0 mol%) were added into a flask containing H<sub>2</sub>O (5 mL) and stirred at room temperature. When the TLC monitoring showed the reaction completion, the catalyst was separated from the reaction mixture and washed with water and EtOH. The product was extracted with ethyl acetate. The organic phase was collected dried over sodium sulfate. Solvent was evaporated and the product was purified using column chromatography using *n*-hexane:ethyl acetate (6:1) as eluent to obtain pure product.

### *Recovery of the nanocatalyst*

The reaction of phenyl bromide (1 mmol) and styrene (1.1 mmol) was selected as a model reaction and was performed in the presence of Pd@Py<sub>2</sub>PZ@MSN catalyst under the optimal reaction conditions. After the reaction completion, the catalyst was separated from the reaction mixture and washed with water and used in the next reaction under the same conditions. The reactions were performed for 10 sequential runs.

## Conclusion

In conclusion, Pd@Py<sub>2</sub>PZ@MSN as a novel catalyst was designed, synthesized and characterized based on the immobilization of palladium onto the modified SBA-15 mesoporous silica nanoparticles. The catalyst was characterized by several methods and the structure of the catalyst was confirmed. The activity of Pd@Py<sub>2</sub>PZ@MSN catalyst was evaluated in Heck and Suzuki reactions. The catalyst showed the best activity in water as solvent in the presence of triethyl amine base. Several substrates with different functionalities were used and, in all cases, the desired compounds were synthesized in good isolated yields. As an advantage, the catalyst showed very good reusability after 10 sequential runs.

## Declarations

### Conflict of interest

The authors declare no conflict of interest.

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## Figures

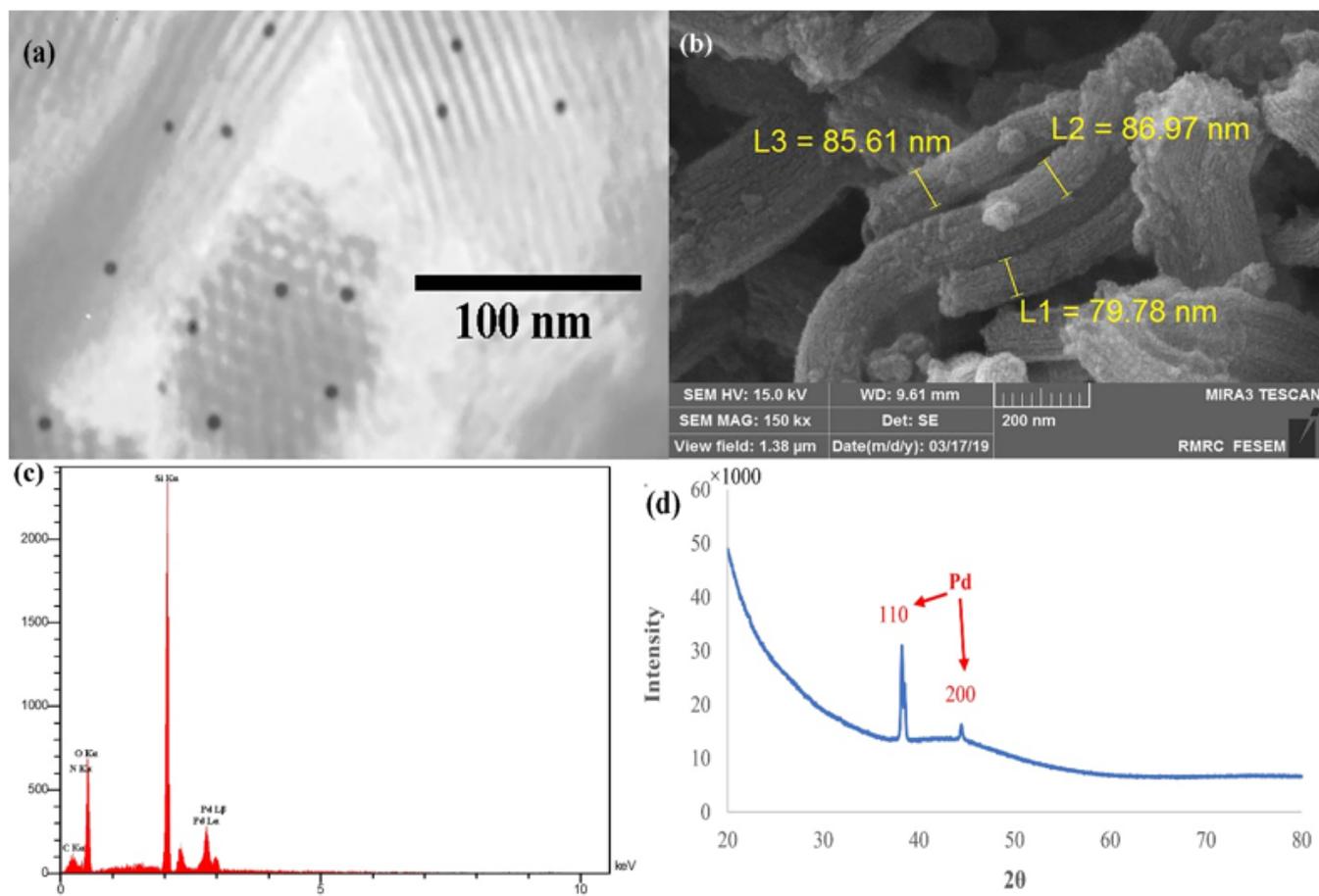


Figure 1

(a) TEM; (b) SEM; (c) EDS; and (d) XRD results of Pd@Py2PZ@MSN catalyst.

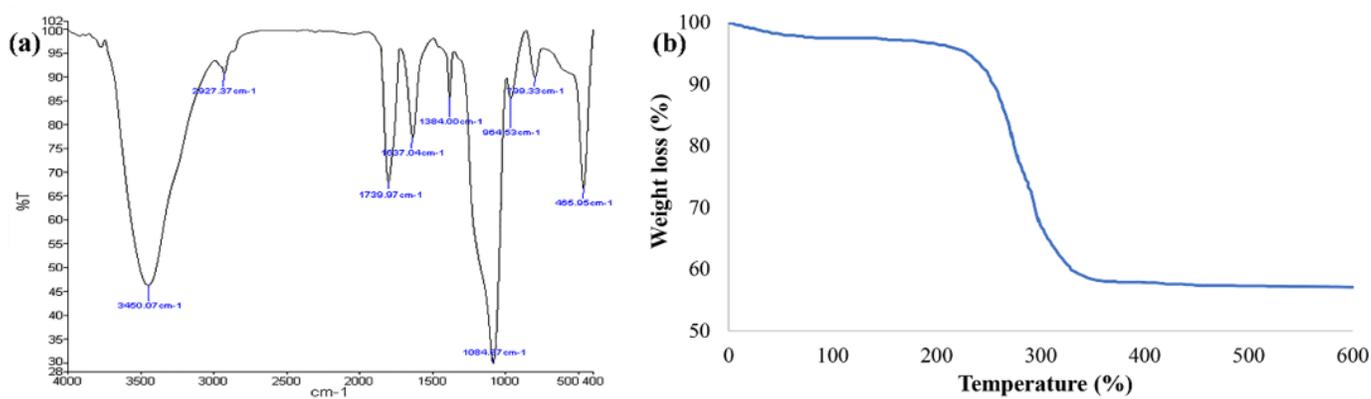
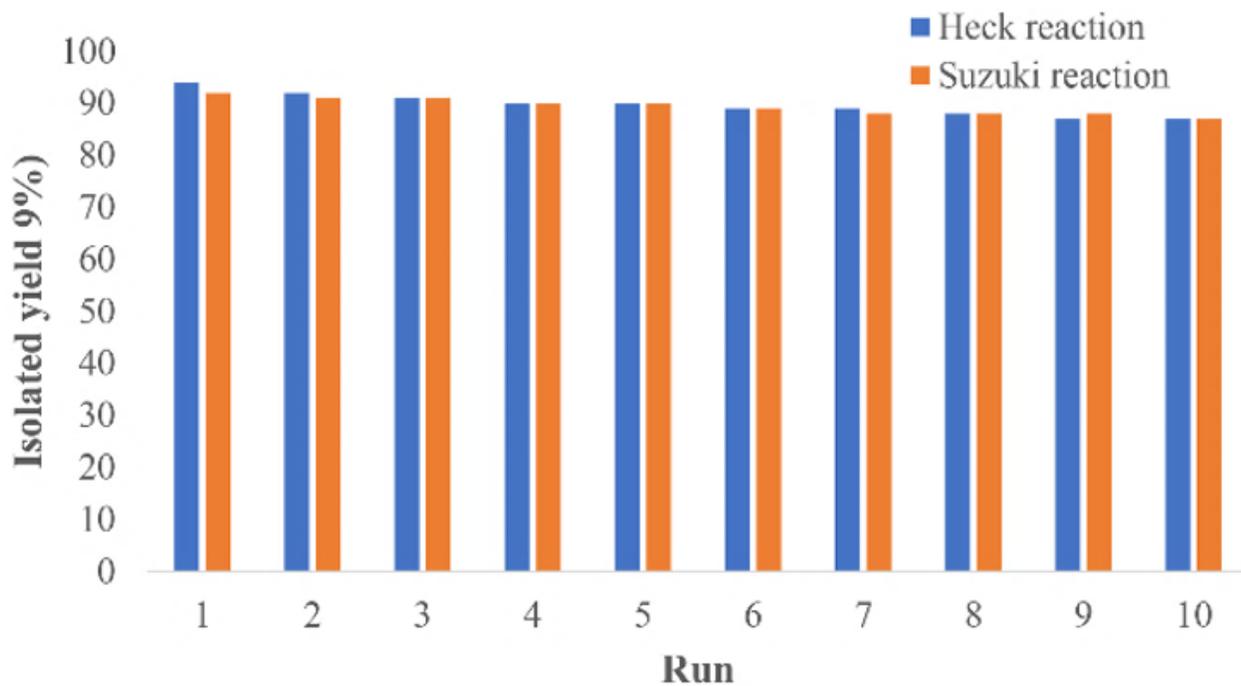


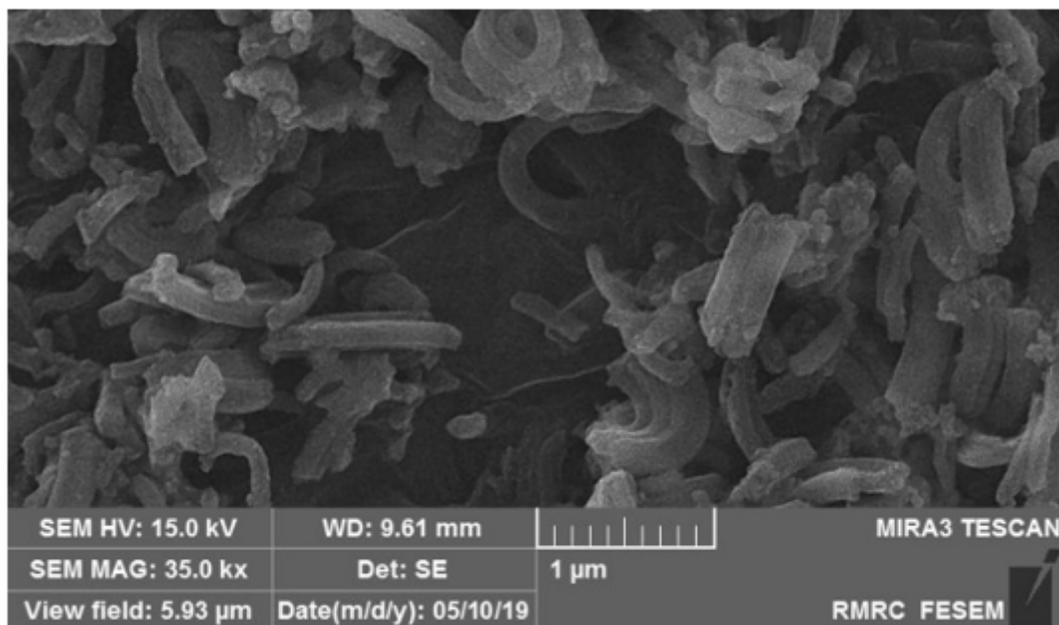
Figure 2

(a) FT-IR; and (b) TGA results of Pd@Py2PZ@MSN catalyst.



**Figure 3**

Recovery results of Pd@Py2PZ@MSN catalyst.



**Figure 4**

SEM image of the recovered Pd@Py2PZ@MSN catalyst.

## Supplementary Files

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